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MARIĆITE, A SODIUM IRON PHOSPHATE, FROM THE BIG FISH RIVER AREA, YUKON TERRITORY, CANADA

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ABSTRACT

Maricite in nodules in sideritic ironstones in the Big Fish River area, Yukon Territory, is colorless, grey, or pale brown, has a white streak, and hardness of 4 to 4½. The measured density is 3.66 g/cm^3. There is no cleavage. Maricite is biaxial negative with $2V$ 43½°, $n\alpha$ 1.676, $n\beta$ 1.695, $n\gamma$ 1.698; dispersion weak, $r>v$; no pleochroism; orientation, $a=X$, $b=Y$. The mineral is orthorhombic, space group *Pmnb*, a 6.867, b 8.989, c 5.049Å; V 311.7Å^3; $Z=4$. The strongest lines in the X-ray powder pattern (Cu$K\alpha$, Guinier camera) are: 3.705(40)(111), 2.729(90)(220), 2.707(80)(211), 2.574(100)(031), 2.525(30)(002), and 1.853(60)(222). The average of six electron microprobe analyses is Na_2O 16.5, MgO 0.8, CaO 0.0, MnO 3.1, FeO 37.4, P_2O_5 42.5, total 100.3 wt. %. This gives $Na_{0.91}Fe_{0.89}Mn_{0.07}Mg_{0.03}P_{1.02}O_{4.00}$ or, ideally, $NaFePO_4$. The name is in honor of Prof. Dr. Luka Maric.

SOMMAIRE

La maricite, qu'on trouve sous forme de nodules dans les minerais de fer sidéritiques de la région de Big Fish River, territoire du Yukon, est incolore, grise ou brun pâle; à rayure branche. Sa dureté est égale à 4 ou 4½. La densité mesurée est de 3.66. La maricite ne possède aucun clivage. Orthorhombique, elle est biaxe négative, $2V$ 43½°, $n\alpha$ 1.676, $n\beta$ 1.695, $n\gamma$ 1.698; la dispersion $r>v$ est faible; il n'y a aucun pléochroïsme; l'orientation est $a=X$, $b=Y$. Le minéral appartient au groupe spatial *Pmnb*, a 6.867, b 8.989, c 5.049Å; V 311.7Å^3; $Z=4$. Les raies les plus intenses du diagramme de poudre (Cu$K\alpha$, chambre de Guinier) correspondent aux espacements suivants: 3.705(40) (111), 2.729 (90) (220), 2.707(80) (211), 2.574(100) (031), 2.525(30) (002) et 1.853(60) (222). La moyenne de six analyses à la microsonde électronique est: Na_2O 16.5, MgO 0.8, CaO 0.0, MnO 3.1, FeO 37.4, P_2O_5 42.5, total 100.3% en poids, ce qui donne la formule calculée $Na_{0.91}Fe_{0.89}Mn_{0.07}Mg_{0.03}P_{1.02}O_{4.00}$ et la formule idéalisée $NaFePO_4$. Le nom du minéral honore le professeur Luka Maric.

(Traduit par la Rédaction)

INTRODUCTION

In addition to the phosphate occurrence in which kulanite (Mandarino & Sturman 1976), baricite (Sturman & Mandarino 1976), and penikisite (Mandarino *et al.* 1977) have been found, another locality about 15 km to the east has yielded some interesting species. The locality is on the Big Fish River at about Latitude 68° 30'N and Longitude 136°30'W, almost at the eastern border of Yukon Territory. Here, as at the kulanite-baricite-penikisite type locality, the rocks are interbedded shales and sideritic ironstones. Although various phosphate minerals occur in fractures in the ironstones, of much greater interest are the nodules which occur in the shale beds. The nodules are variable in size and some are as large as 15 cm. Many consist of pyrite whereas others are made up of various phosphates. Some of the phosphate nodules are megascopically monomineralic, but others contain several species.

A few nodules consist almost entirely of maricite, but most specimens studied have the following species in direct contact with maricite: quartz, ludlamite, vivianite, pyrite, wolfeite, a member of the apatite group, a member of the varulite group, and a new species. Examination of thin sections of nodules which appeared to consist mainly of maricite revealed that ludlamite, quartz, and vivianite occur as very small inclusions within the maricite and along fractures. Other minerals in the immediate area are: lazulite, childrenite, and siderite. Maricite was approved by the Commission on New Minerals and Mineral Names, IMA. It is named in honor of Prof. Dr. Luka Marić, long-time head of the Department of Mineralogy and Petrology, University of Zagreb. Type material (grams) is preserved in the collections of the Royal Ontario Museum (ROM No. M34241) and the Mineralosko-Petrografski Musej in Zagreb, Jugoslavia. The name is pronounced MĀ RĬCHAIT.

Physical and Optical Properties

Maričite is colorless to grey and, occasionally, pale brown. It has a white streak, vitreous lustre, is transparent to translucent, and has no cleavage. The mineral does not fluoresce in either short-wave or long-wave ultraviolet light. The hardness is 4 to 4½. The density measured with a Berman microbalance is 3.66(2) g/cm³. The density calculated for $Na_{0.91}(Fe_{0.89}Mn_{0.07}Mg_{0.03})P_{1.02}O_{4.00}$ (derived from the average of 6 electron microprobe analyses) is 3.64 g/cm³. For $Na(Fe_{0.90}Mn_{0.07}Mg_{0.03})PO_4$ the calculated density is 3.68 g/cm³.

Maričite is biaxial negative with $2V$(meas.) 43½°, $2V$(calc.) 43.0°, $n\alpha$ 1.676(2), $n\beta$ 1.695(2), $n\gamma$ 1.698(2) for sodium light. Dispersion is weak $r>v$. The mineral is non-pleochroic. Orientation is $a=X$, $b=Y$. The DTA curve shows a small exothermic peak at 505°C.

Crystallography

The specimens used in this study contained no euhedral crystals. Instead, the nodules consisted of elongate grains in a radiating to sub-parallel structure. Elongation of these grains was later shown to be [100]. Many of the individual grains had what appeared to be crude crystal faces parallel to [100]. However, we could not obtain angular measurements of sufficient accuracy to assign reasonable Miller indices to these planes. On the other hand, LePage & Donnay (1977) recognized the following forms on the specimen used for the structure determination: {010}, {011}, {012}, and {032}.

Weissenberg and precession studies of maričite showed that the mineral is orthorhombic with space group *Pmnb* or *P2₁nb*. The latter space group was eliminated by the structure determination of Le Page & Donnay (1977). The unit cell, which is compared with the parameters obtained by LePage & Donnay in Table 1, contains 4[$NaFePO_4$].

The X-ray powder diffraction data are given in Table 2. Intensities were estimated visually by the technique described in Mandarino *et al.* (1977). Patterns from five different fragments were produced using Cu$K\alpha$ radiation and a Guinier camera. All the patterns were practically identical.

Chemical Composition

The chemical composition of maričite was determined using an Applied Research Laboratories – AMX electron microprobe equipped with a Tracor-Northern NS-880 energy-dispersive spectrometer. Operating conditions were: accelerating voltage 15 kV; sample current about 1.5 nanoamperes; beam diameter about 2 microns.

Overlapping spectra were unravelled with a multiple least-squares fitting technique (program ML, written by F. Schamber, Tracor-Northern Ltd.). In order to use this analytical method, it is necessary to have standard spectra which are themselves free of overlapping peaks. These spectral standards for this series of analyses were: Na–NaCl; Mg–MgO; P–$Ca_2P_2O_7$; Ca–$CaAl_2Si_2O_8$; Mn–Mn-metal; Fe–Fe_2SiO_4. Apparent concentrations ('k' values) for Na, Mn, and Fe were calculated with reference to the analytical standard riebeckite R2535, previously

TABLE 1. CRYSTALLOGRAPHIC DATA FOR MARIĆITE, $NaFePO_4$

	Orthorhombic	Space group *Pmnb*		$Z = 4$
	ROM specimen M34241			ROM specimen M34506
	Single-crystal diffractometer*	Precession and Weissenberg data	Refined from Guinier data (Table 2)	Refined from Guinier data
a (Å)	6.861(1)	6.86	6.867(1)	6.864(2)
b (Å)	8.987(1)	9.02	8.989(2)	8.994(2)
c (Å)	5.045(1)	5.05	5.049(1)	5.049(1)
V (Å³)	311.1	312.5	311.7	311.7

*Refinement by LePage & Donnay (1977); all others this study

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR MARIĆITE

I	d_{obs}	d_{calc}	hkl	I	d_{obs}	d_{calc}	hkl
5	4.50	4.495	020				
20	4.40	4.402	011	15	1.714	1.717	400
						1.711	331
10	3.757	3.761	120	1	1.696	1.694	051
40	3.705	3.706	111	2	1.678	1.679	042
90	2.729	2.728	220	5	1.654	1.654	013
80	2.707	2.707	211	1	1.598	1.599	411
100	2.574	2.577	031	10	1.519	1.519	251
30	2.525	2.525	002	15	1.508	1.508	242
15	2.431	2.430	012	1	1.499	1.498	060
10	2.401	2.400	221	15	1.490	1.490	213
1	2.244	2.247	040			1.467	033
1	2.200	2.201	022	7	1.466	1.464	052
10	2.096	2.096	122			1.464	160
1	2.086	2.085	301	5	1.429	1.429	431
2	2.062	2.061	231	5	1.420	1.420	402
30	1.881	1.880	240	5	1.288	1.288	062
60	1.853	1.853	222				

CuKα radiation, Guinier camera.

TABLE 3. ELECTRON MICROPROBE ANALYSES OF MARIĆITE

	Analyses							Calculated Analyses*	
wt%	1	2	3	4	5	6	Avg.	A	B
Na_2O	16.4	16.0	16.4	16.7	16.2	17.3	16.5	17.9	17.83
MgO	0.9	0.9	0.8	0.8	1.0	0.5	0.8	0.7	
CaO	0.0	0.0	0.0	0.0	0.0	0.1	0.0		
MnO	3.0	2.9	3.2	3.0	3.0	3.2	3.1	2.9	
FeO	37.2	37.9	37.4	37.3	36.8	37.7	37.4	37.4	41.34
P_2O_5	41.8	41.5	41.4	43.5	43.5	43.5	42.5	41.1	40.83
Total	99.3	99.2	99.2	101.3	100.5	102.3	100.3	100.0	100.00

Dr. M.I. Corlett, analyst. See text for operating conditions and details.
Formula from average of six analyses, based on 4 oxygen ions:
$Na_{0.91}(Fe_{0.89}Mn_{0.07}Mg_{0.03})_{\Sigma=0.99}P_{1.02}O_{4.00}$

* A: calculated for $Na(Fe_{0.90}Mn_{0.07}Mg_{0.03})PO_4$
B calculated for $NaFePO_4$

analyzed using wet-chemical and wavelength-dispersive methods (Rucklidge *et al.* 1971). MgO, $Ca_2P_2O_7$, and $CaAl_2Si_2O_8$ were used as the analytical standards, as well as the spectral standards, for Mg, P, and Ca, respectively.

Apparent concentrations thus obtained were then corrected for absorption, secondary fluorescence, and atomic-number effects using a general ZAF correction program. Analytical data were obtained from six points in a thin section. The results are given in Table 3. The chemical formula derived from the average of the six analysis is $Na_{0.91}(Fe_{0.89}Mn_{0.07}Mg_{0.03})P_{1.02}O_{4.00}$. This and its idealized equivalent, $Na(Fe_{0.90}Mn_{0.07}Mg_{0.03})PO_4$, are close to $NaFePO_4$. The temptation to structurally relate maricite to triphylite ($LiFePO_4$), natrophilite ($NaMnPO_4$), or lithiophilite ($LiMnPO_4$) is great. Although maricite has the same space group as these three minerals *(Pmnb)*, the unit-cell parameters and the structure types are different (LePage & Donnay 1977).

The specific refractive energy calculated from the Gladstone-Dale equation, the average chemical analysis, and the constants given by Mandarino (1976) is 0.184. The value calculated from the refractive indices and the measured density is 0.189.

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